

## Influence of Carbide Phases on the Corrosion Behavior of Amorphous Chromium Electrodeposits

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Chromium coatings are extensively used in various industrial branches for corrosion and erosion protection of metal parts. These coatings are usually deposited from standard chrome-plating baths based on  $\text{CrO}_3$ . Taking into account the pressing environmental requirements to the safety of electroplating waste, the further use of electrolytes containing Cr(VI) becomes ecologically unacceptable. From this viewpoint, the studies aimed at deposition of chromium electroplates of high quality from Cr(III) baths is quite promising. The prospects of these studies are also economically warranted. This work presents the results on the preparation methods of high-quality chromium electroplates from Cr(III) baths, their corrosion and electrochemical behavior, and also on the linkage between these properties and the deposit composition and structure.

The main obstacles met during chromium deposition from Cr(III) electrolytes are associated with the outstanding stability of its aqua-complexes. The use of polydentate ligands that replace water molecules from the inner coordination sphere of chromium aqua-complexes and provide a sufficiently high rate of inner-sphere transfer of electrons allowed the development of sulfate—oxalate Cr(III) baths of different compositions (see [1, 2] and references therein). An example is the following composition (g/l):  $\text{Cr}_2(\text{SO}_4)_3 \cdot 6\text{H}_2\text{O}$ , 100—200;  $\text{Na}_2\text{C}_2\text{O}_4$ , 15—35;  $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ , 100;  $\text{Na}_2\text{SO}_4$ , 80; pH 1.1—2.1. The optimal temperature is 35—40°C. The deposition rate reaches 2  $\mu\text{m}/\text{min}$ , and the current efficiency exceeds 40%. The appearance and brightness of obtained deposits compares well with coatings electroplated from commercial baths.

The studies of corrosion and electrochemical properties of the deposits were carried out by measuring steady-state polarization curves in solutions of 0.5 mol/l  $\text{H}_2\text{SO}_4$ . The deposits 10—40- $\mu\text{m}$  thick, which were electroplated on copper or brass supports, were tested. The electrochemical studies showed that the deposits, being anodically polarized, exhibit no region of active chromium dissolution, and the current-less potential is shifted in the positive direction as compared with metallurgical chromium and chromium electroplates deposited from standard baths and located in the passivity region. A comparison of our results with literature data has shown that the aforementioned corrosion behavior of chromium electroplated from sulfate—oxalate Cr(III) baths correlates well on a qualitative level with the behavior of chromium deposits obtained from standard Cr(VI) baths with additions of formic acid ( $c_{\text{HCOOH}} \geq 0.22$  mol/l) [3, 4]. To explain this similarity, we examined the structure and phase composition of the electroplates, and also their surface composition, before and after anodic polarization in sulfuric-acid solutions.

XRD studies revealed an amorphous structure of electroplates deposited from sulfate—oxalate Cr(III) baths. X-

ray microanalysis and XPS technique showed the deposits to contain 6.5—7 wt % carbon in the form of  $\text{Cr}_{23}\text{C}_6$  carbide and partially as the products of oxalic-acid reduction. It should be noted that a substantial amount of carbon was also detected in amorphous chromium deposits obtained from Cr(VI) baths containing formic acid [3—7], formamide, formaldehyde, and glyoxal [6].

The results obtained in our work [8] and analysis of literature data allowed us to propose that carbide compounds of chromium appear in the studied deposits due to the reduction of oxalic acid, which proceeds on newly formed chromium in parallel with the discharge of metal ions. An important additional argument confirming this hypothesis is the result of analyzing the XPS characteristics of metallurgical-chromium surface after its exposure to sulfuric-acid solutions containing organic substances (oxalic acid, dimethylformamide, and methanol). The band C1s of these spectra demonstrated the features typical of the presence on the surface of the products of deep reductive destruction of organic substances (carbon particles and carbon containing functional groups) [9].

Carbide compounds of chromium are known to exhibit a sufficiently low hydrogen-evolution overpotential [10]. Apparently, the presence of these compounds in the studied deposits should shift the current-less potential of the electroplates in the positive direction to the passivity region, i.e., will cause the very effect that is observed experimentally. In other words, the fact that chromium electroplates deposited from Cr(III) baths (and probably those from Cr(VI) baths containing certain organic substances) are self-passivated in sulfuric acid solutions suggests that their composition includes carbide compounds which behave as cathodic additives.

Another fundamental conclusion, which follows from this study, is the fact that chromium should be considered as a metal exhibiting electrocatalytic activity in cathodic processes toward organic substances.

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